Copper(I) Promoted Dechlorinative Surzur-Tanner Rearrangement of 2,2,2-Trichloroethyl Carboxylates

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Supporting Information

Experimental Procedures

1. Peparation of 2,2,2-trichloroethyl esters

These were prepared by acylation of 2,2,2-trichloroethanol with acyl chlorides following the reported[1] procedure with some modifications.

1.1. 2,2,2-Trichloroethyl cinnamate, **1a:** A mixture of cinnamic acid (7.4g, 0.05 mol) and thionyl chloride (9.5g, 6 ml, 0.08 mol) was refluxed for 2 hours. The excess of thionyl chloride was removed by distillation. The trace amount of the thionyl chloride that remained was removed by aspirator to give crude cinnamoyl chloride which was used as such for preparation of the ester.

A solution of cinnamoyl chloride in dichloromethane (20 ml) was added slowly (10 min.) to a stirred mixture of 2,2,2-trichloroethanol (7.4g, 0.05 mol), dichloromethane (30 ml) and anhydrous potassium carbonate (6.9g, 0.05 mol) cooled in an ice bath (5-10^{o}C). After the addition was complete, the reaction mixture was stirred at room temperature for 6 hours. The solid was filtered and washed with dichloromethane. The filtrate was diluted with some more dichloromethane (50 ml), washed successively with saturated sodium bicarbonate solution (2×20 ml), water (3×30 ml) and brine (20 ml). The organic layer was dried over anhydrous sodium sulphate and filtered. The solvent was evaporated from the filtrate to get the crude ester. This was dissolved in minimum amount of methanol and to it water was added slowly with stirring with a glass rod until some turbidity appeared, then immediately it was cooled in an ice bath to get 11.2g (80%) of **1a** as colourless crystals, m.p. 46^{o}C (Lit[1] b.p. 112^{o}C/15 torr).

1.2. 2,2,2-Trichloroethyl benzoate,[2] **1b:** To a solution of 2,2,2-trichloroethanol (3.0g, 0.02 mol) and triethylamine (3ml, 0.02 mol) in tetrahydrofuran (40 ml) cooled in an ice bath to 2-5^{o}C was added benzoyl chloride (3g, 2.5 ml, 0.021 mol) drop wise with stirring over 10 minutes. The reaction mixture was stirred at room temperature for 6 hours, filtered and washed with tetrahydrofuran. The solvent was evaporated from the filtrate and the residue was taken up in ether (100 ml), washed successively with dilute hydrochloric acid (2×20 ml) and saturated sodium bicarbonate solution (2×20 ml). The organic layer was dried over anhydrous sodium sulphate and filtered. Evaporation of the solvent gave the crude ester, which was purified by column chromatography on silica gel column using 1-2% ethyl acetate in hexane as the mobile phase to give 4.1g (81%) of pure **1b**.

1.3. 2,2,2-Trichloroethyl 3-methylbut-2-enoate, **1c:** A mixture of 3-methyl-butenoic acid (1.7g, 0.017 mol) and thionyl chloride (1.8 ml, 0.025 mol) was refluxed for 1.5 hours and excess of thionyl chloride was removed as usual. A solution of this crude acid chloride in dichloromethane (10 ml) was added to a stirred mixture of 2,2,2-trichloroethanol (2.2g, 0.015 mol) and anhydrous potassium carbonate (2.4g, 0.017 mol) in dichloromethane (20 ml) cooled in an ice bath to 2-5^{o}C. The reaction mixture was stirred at room temperature for 6 hours. The solid was filtered and washed with dichloromethane. The filtrate was washed successively with saturated sodium bicarbonate solution (2×30 ml) and brine (20 ml), dried over anhydrous sodium sulphate and filtered. The solvent was evaporated from the filtrate to get the crude ester, which was purified on silica gel column by eluting with 4% ethylacetate in hexane to get 2.6g (75%) of the pure ester **1c** as colourless liquid.

1.4. 2,2,2-Trichloroethyl dodecanoate,[3] **1d:** Dodecanoyl chloride was prepared from dodecanoic acid (4.0g, 0.02 mol) and thionyl chloride (3.6g, 0.03 mol) as described earlier. The reaction time required was 3 hours.

To a stirred solution of 2,2,2-trichloroethanol (2.7g, 0.018 mol) and triethylamine (3ml, 2.1g, 0.021 mol) in dichloromethane (10 ml) was added slowly over 10 minutes, a solution of the crude acid chloride obtained above. The reaction mixture was stirred for 8 hours at room temperature. The solid was removed by filtration. The filtrate was washed successively with dilute hydrochloric acid (2×30 ml) and

saturated sodium bicarbonate solution (2×30 ml) and kept over anhydrous sodium sulphate. Filtration and evaporation of the solvent gave the crude ester, which was purified on silica gel column by eluting with 3% ethylacetate in hexane to get the ester **1d** as colourless liquid (5.4g, 90%).

1.5. 2,2,2-Trichloro-1-phenylethyl cinnamate, **1e:** 2,2,2-Trichloro-1-phenyl ethanol was prepared by the Grignard reaction of phenylmagnesium bromide with chloral. Cinnamate of this alcohol was prepared by acylation of 2,2,2-trichloro-1-phenylethanol (4.51g, 0.02 mol) with cinnamoyl chloride {prepared from 3.1g (0.21 mol) of cinnamic acid} over anhydrous potassium carbonate (4.5g, 0.02 mol) in dichloromethane following the same procedure as described under section 1.1. The reaction time was 48 hours at room temperature. The product was recrystallised from hexane to give **1e** as colourless crystals (4.3g, 60%), m.p. 95^{o}C.

1.6. 2,2,2-Trichloro-1-phenylethyl benzoate, **1f:** This ester was prepared from benzoyl chloride (2.3g, 0.016 mol), 2,2,2-trichloro-1-phenyl ethanol (3.4g, 0.015 mol), triethylamine (2.2 ml, 1.6g, 0.016 mol) in tetrahydrofuran (40 ml) as described under section 1.2. The reaction time was 48 hours, at room temperature. The product was recrystallised from hexane to get **1f** as colourless crystals (3.1g, 63%), m.p. 96-97^{o}C.

1.7. 2,2,2-Trichloro-1-phenylethyl acetate, **1g:** To a mixture of 2,2,2-trichloro-1-phenylethanol (3.4g, 0.015 mol) and DMAP (0.2g, 1.5 mmol) in pyridine (1.6g, 0.02 mol) cooled to 0^{o}C, acetic anhydride (3g, 0.03 mol) was added and the reaction mixture was stirred at room temperature for 3 hours. It was taken up in ether washed successively with water (3×30 ml), dilute hydrochloric acid (2×20 ml) and saturated sodium bicarbonate solution (3×30 ml) and dried over anhydrous sodium sulphate. Filtration and evaporation of solvent gave the crude ester, which was recrystallised from hexane to get the pure ester **1g** as colourless crystals (3.5g, 88%), m.p. 85-87^{o}C (Lit.[4] m.p. 86^{o}C).

1.8. 2,2-Dichloroethyl benzoate (257): It was prepared from 2,2-dichloroethanol (1.7g, 0.015 mol), benzoyl chloride (2.2g, 0.016 mol) and triethylamine (2.2 ml, 0.016 mol) in tetrahydrofuran (40 ml) as described under section 5.3.1.2. The crude product was purified on silica gel column by eluting with 1-2% ethylacetate in hexane to get the ester as colourless liquid[191] (3.1g, 94%).

2. Rearrangement of 2,2,2-trichloroethyl esters, **1a-g: General procedure:** In a two necked round bottomed flask fitted with a reflux condenser and a rubber septum was created oxygen free nitrogen atmosphere using Schlenk technique. A mixture of 2,2,2-trichloroethyl ester **1** (1 mmol) and CuCl (0.2g, 2 mmol) was added quickly into the flask. It was immediately followed by addition of 0.32g (2 mmol) of 2,2'-bipyridine dissolved in 8 ml of degassed dichloroethane through the rubber septum using a syringe. The reaction mixture was heated at reflux with stirring. The progress of the reaction was monitored by TLC. After the reaction was complete (2-4 hours), the reaction mixture was cooled and filtered. The filtrate was evaporated under reduced pressure and the crude product, thus obtained, was purified on silica gel column by eluting with 1-4% ethylacetate in hexane to get the pure product **2** in 84-98% yields.

3. Hydrolysis of 1-chloro-2-phenylethenyl benzoate, **2f:** A solution of **2f** (0.08g, 0.31 mmol), K_2CO_3 (0.17g, 1.2 mmol), water (1 ml) in dioxane (5 ml) was refluxed with stirring for 12 hours. The solvent was evaporated from the reaction mixture and the residue was diluted with water. The aqueous solution was washed with ether (2×20 ml), acidified with dilute sulphuric acid and extracted with ether (3×30 ml). The combined ether extract was dried over sodium sulphate. Filtration and evaporation gave a pale yellow coloured solid 0.07g, which was found by NMR to be a mixture (approximately 1:1) of benzoic acid and phenylacetic acid.

4. Acid hydrolysis of 1-chloro-2-phenylethenyl acetate, **2g:** The compound **2g** (0.05g, 0.25 mmol) was heated at reflux with stirring in moderately dilute sulphuric acid (3 ml, pH~0.5) for 3 hours. The reaction mixture was extracted with ether (3×20 ml). The combined ether layer was washed with saturated sodium bicarbonate solution (3×15 ml). The combined bicarbonate extract was acidified with conc. hydrochloric acid and extracted with ether (3×20 ml). The combined ether extract was washed with brine (10 ml) and dried over anhydrous sodium sulphate. Filtration and evaporation of ether gave phenylacetic acid (0.034g, 98%) as an almost colourless solid, m.p.74-75^{o}C, (Lit.[6] m.p. 76.5^{o}C). A mixture of this sample with equal amount of an authentic phenylacetic acid melted at 75^{o}C.

5. Base hydrolysis of 1-chloro-2-phenylethenyl acetate, **2g:** The compound **2g** (0.03g, 0.153 mmol) was heated with 2 ml of sodium hydroxide solution (5%) at 50^{o}C for 1 hour. The reaction mixture was cooled and washed with ether (2×20 ml). The alkaline solution was acidified with conc. hydrochloric acid and extracted with ether (3×20 ml). The combined ether extract was washed with brine (10 ml) and dried over anhydrous sodium sulphate. Filtration and evaporation of ether gave phenylacetic acid as an almost colourless solid, 0.02g (96%), m.p. 74^{o}C (Lit.[6] m.p. 76.5^{o}C). A mixture of this sample with equal amount of an authentic phenylacetic acid melted at 74-75^{o}C.

6. Cross over experiment with 2,2,2-trichloroethyl dodecanoate, **1d and 2,2,2-Trichloro-1-phenylethyl cinnamate**, **1e:** In a two necked round bottomed flask fitted with a reflux condenser and a rubber septum was created oxygen free nitrogen atmosphere using Schlenk technique. A mixture of **1e** (0.36g, 1 mmol) and CuCl (0.4g, 4 mmol) was added quickly into the flask, which was immediately followed by the addition of a solution of **1d** (0.33g, 1 mmol) and 2,2'-bipyridine (0.64g, 4 mmol) in 8 ml of degassed 1,2-dichloroethane through the rubber septum using a syringe. The reaction mixture was heated at reflux with stirring for 4 hours. Then it was cooled, filtered and evaporated to give the crude product (TLC of the crude product showed only two spots), which was purified by column chromatography on silica gel column. The first product, which was eluted with 2% ethylacetate in hexane was found to be **2d** (0.23g, 88%). The other product, which got eluted with 4% ethylacetate in hexane as colourless solid, was identified as **2e** (0.22g, 77%), m.p. 77^{o}C. Melting point (77-78^{o}C) of a mixture of this sample with **2e** obtained under section 2 showed no depression.

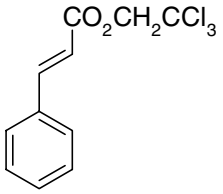
7. Reaction of 2,2,2-Trichloroethyl cinnamate, **1a and 2,2,2-Trichloroethyl dodecanoate**, **1d with tributyltin hydride:** (a) *Reaction of* **1d** *with 2.5 equiv. of tributyltin hydride:* In a two necked round bottomed flask fitted with a reflux condenser and a rubber septum was created oxygen free nitrogen atmosphere using Schlenk technique. A solution of **1d** (0.33g, 1 mmol, 0.1 M) and AIBN (0.016g, 0.1 mol) in 10 ml of benzene was introduced into the flask and heated to reflux with stirring. A solution of tributyltin hydride (0.73g, 2.5 mmol, 0.25 M) in 10 ml of benzene was added slowly through a syringe into the refluxing solution over a period of 1.5 hour and the refluxing was continued for a further period of 2.5 hours. The reaction mixture was cooled and the solvent was evaporated. The residue was purified by column chromatography on a silica gel column to get pure 2-chloroethyl dodecanoate, **6** (0.25g, 95%) as a colourless liquid, which came on elution with 2% ethylacetate in hexane.

(b) *Reaction of* **1a** *and* **1d** *with 1.5 equiv. of tributyltin hydride:* In a two necked round bottomed flask fitted with a reflux condenser and a rubber septum was created oxygen free nitrogen atmosphere using Schlenk technique. A solution of **1d** (0.33g, 1 mmol, 0.04 M) or **1a** (0.28g, 1 mmol, 0.04 M) and AIBN (0.01g, 0.06 mol) in 25 ml of benzene was injected into the flask. The solution was heated to reflux with stirring and a solution of tributyltin hydride (0.44g, 1.5 mmol, 0.075 M) and AIBN (0.01g, 0.06 mol) in 20 ml of benzene was added slowly through a syringe during a period of 4 hours. The heating at reflux was continued for a further period of 2 hours. The reaction mixture was cooled and the solvent was evaporated. The residue was subjected to silica gel column chromatography for purification. The reaction of **1d** yielded 2,2-dichloroethyl dodecanoate **7** (0.24g, 81%) as colourless liquid, which was eluted with 1-2% ethylacetate in hexane. The reaction of **1a** gave 2,2-dichloroethyl cinamate **8** (0.18g, 74%) as colourless liquid, which was collected from the column by eluting with 1% ethylacetate in hexane.

8. Reaction of 1a with CuCl/bpy in the presence of tributyltin hydride: In a two necked round bottomed flask fitted with a reflux condenser and a rubber septum was created oxygen free nitrogen atmosphere using Schlenk technique. A mixture of **1a** (0.28g, 1 mmol) and CuCl (0.2g, 2 mmol) was added quickly into the flask, which was followed by the addition of a solution of 2,2'-bipyridine (0.32g, 2 mmol) and tributyltin hydride (0.44g, 1.5 mmol) in 10 ml benzene (0.15 M in tributyltin hydride and 0.1 M in **1a**). The reaction mixture was heated to reflux with stirring for 5 hours. The reaction mixture was cooled, filtered and evaporated to get a mixture of crude products, which was cleaned up from the copper and tin compounds by silica gel column chromatography. Elution with 1% ethylacetate in hexane gave a colourless liquid (0.204g) containing the rearranged product **2a**, reduced product **8** and some starting compound **1a** in a ratio of **2a : 8 : 1a =** 79 : 18 : 3 along with some amount of organotin compounds as impurity as determined by ^{1}H NMR analysis.

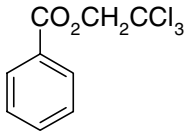
9. Physical and spectral data

2,2,2-Trichloroethyl cinnamate, **1a**



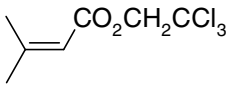
Colourless crystals (aq. methanol), m.p. 46°C (Lit.[1] b.p. 112°C/15 torr.). IR: ν_{max} 3060 (w), 2954 (w), 1718 (s, ester C=O), 1637 (s, C=C), 1312 (s), 1164 (s) cm^{-1}. ^1H NMR: δ 4.88 (s, 2H), 6.54 (d, 1H, J = 16.01 Hz), 7.42 (m, 3H), 7.57 (m, 2H), 7.83 (d, 1H, 16.01 Hz) ppm. ^{13}C NMR: δ 73.95, 95.10, 116.22, 128.25, 128.85, 130.72, 133.85, 146.89, 164.95 ppm. MS (m/z): 278 (M^+), 280 (M^+-Cl), 131 ($PhCH=CHCO^+$, base peak), 103, 77. Analysis: Calculated for $C_{11}H_9O_2Cl_3$: C 47.26, H 3.24%. Found C 47.35; H 3.28%.

2,2,2-Trichloroethyl benzoate, **1b**



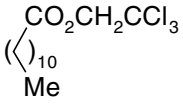
Colourless liquid.[2] IR: ν_{max} 2954 (w), 1736 (s, ester C=O), 1264 (s), 1117 (s) cm^{-1}. ^1H NMR: δ 4.97 (s, 2H), 7.49 (m, 2H), 7.62 (m, 1H), 8.13 (m, 2H) ppm. MS (m/z): 252 (M^+), 253 (M^++1), 130, 104 (base peak), 76.

2,2,2-Trichloroethyl 3-methylbut-2-enoate, **1c**



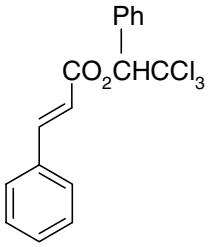
Colourless liquid. IR: ν_{max} 2949 (s), 1732 (s, ester C=O), 1650 (s, C=C), 1221 (s) cm^{-1}. ^1H NMR: δ 1.96 (s, 3H), 2.22 (s, 3H), 4.76 (s, 2H), 5.81 (s, 1H) ppm. ^{13}C NMR: δ 20.47, 27.49, 73.37, 95.42, 114.52, 159.93, 164.25 ppm. MS (m/z): 230 (M^+), 195, 130, 99, 82 (base peak), 55.

2,2,2-Trichloroethyl dodecanoate, **1d**



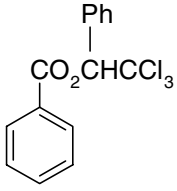
Colourless liquid.[3] IR: ν_{max} 2923 (s), 2854 (s), 1751 (s, ester C=O), 1147 (s) cm^{-1}. ^1H NMR: δ 0.88 (t, 3H, J = 6.56 Hz), 1.26 (bs, 16H), 1.69 (quintet, 2H, J = 7.25 Hz), 2.46 (t, 2H, J = 7.47 Hz), 4.74 (s, 2H) ppm. MS (m/z): 330 (M^+), 331 (M^++1), 332 (M^++2), 333 (M^++3), 294 (M^+-HCl), 130, 85, 73, 71, 60, 57, 43 (Me_2CH^+, base peak).

2,2,2-Trichloro-1-phenylethyl cinnamate, **1e**



Colourless crystals (hexane), m.p. 95°C. IR: ν_{max} 3068 (w), 2965 (w), 1719 (s, ester C=O), 1635 (s, C=C), 1334 (s), 1151 (s) cm^{-1}. ^1H NMR: δ 6.50 (s, 1H), 6.58 (d, 1H, J = 16.00 Hz), 7.40 (m, 6H), 7.58 (m, 2H), 7.68 (m, 2H), 7.82 (d, 1H, J = 16.00 Hz) ppm. ^{13}C NMR: δ 82.63, 99.43, 116.55, 127.90, 128.30, 128.89, 129.63, 130.75, 133.16, 133.93, 146.90, 164.49 ppm. MS (m/z): 277 (M^+-Ph), 130 (base peak), 103, 77; Analysis: Calculated for $C_{17}H_{13}O_2Cl_3$: C 57.41, H 3.68%. Found C 57.90; H 3.72%.

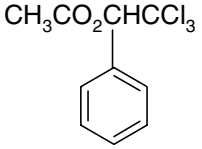
2,2,2-Trichloro-1-phenylethyl benzoate, **1f**



Colourless crystals (hexane), m.p. 96-97°C. IR: ν_{max} 3033 (m), 2952 (m), 1727 (s, ester C=O), 1260 (s) cm^{-1}. ^1H NMR: δ 6.59 (s, 1H), 7.40 (m, 3H), 7.49 (t, 2H, J = 7.58 Hz), 7.62 (t, 1H, J = 7.36 Hz), 7.71 (d, 2H, J = 5.27 Hz), 8.17 (d, 2H, J = 7.51 Hz) ppm. ^{13}C NMR: δ 83.14, 99.44, 127.97, 128.61, 128.96, 129.58, 129.79, 130.02, 133.10, 133.73, 164.21 ppm. Analysis: Calculated for $C_{15}H_{11}O_2Cl_3$: C 54.66, H 3.36%. Found C 54.41, H 3.48%.

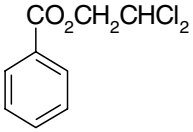
2,2,2-Trichloro-1-phenylethyl acetate, **1g**

Colourless crystals (hexane), m.p. 85-87°C (Lit.[4] m.p. 87-88°C). IR: ν_{max} 3069 (w), 2952 (w), 1756 (s), 1740 (s), 1225 (s) cm^{-1}. ^1H NMR: δ 2.24 (s, 3H), 6.40 (s, 1H), 7.43 (m, 3H), 7.64 (m, 2H) ppm. ^{13}C NMR: δ 20.75, 82.51, 99.28, 127.91, 129.64, 133.05, 168.62 ppm. Analysis: Calculated for $C_{10}H_9O_2Cl_3$: C 44.89, H 3.39%. Found C 44.32,



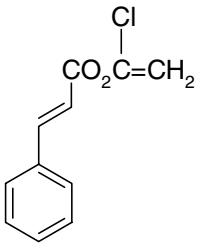
H 3.58%.

2,2-Dichloroethyl benzoate



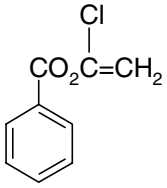
Colourless liquid. [191] IR: ν_{max} 3064 (w), 2954 (w), 1732 (s, ester C=O), 1267 (s), 1117 (s) cm^{-1}. ^1H NMR: δ 4.68 (d, 2H, J = 5.99 Hz), 5.98 (t, 1H, J = 5.99 Hz), 7.46 (m, 2H), 7.59 (m, 1H), 8.07 (m, 2H) ppm.

1-Chloroethenyl cinnamate, **2a**



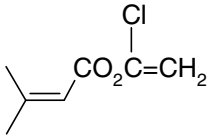
Viscous liquid. IR: ν_{max} 3062 (w), 3030 (w), 1748 (s, ester C=O), 1633 (s, C=C), 1104 (s) cm^{-1}. ^1H NMR: δ 5.12, 5.16 (AB quartet, 2H, J = 2.94 Hz), 6.46 (d, 1H, J = 16.00 Hz), 7.42 (m, 3H), 7.56 (m, 2H), 7.82 (d, 1H, J = 16.00 Hz) ppm. ^{13}C NMR: δ 103.95, 115.54, 128.43, 129.03, 131.12, 133.73, 140.77, 148.17, 163.04 ppm. Analysis: Calculated for $C_{11}H_9O_2Cl$: C 63.32, H 4.35%. Found C 63.26, H 4.84%.

1-Chloroethenyl benzoate, **2b**



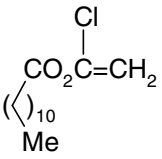
Colourless liquid. IR: ν_{max} 3065 (w), 1756 (s, ester C=O), 1643 (s, C=C), 1261 (s) cm^{-1}. ^1H NMR: δ 5.17, 5.21 (AB quartet, 2H, J = 2.87 Hz), 7.48 (t, 2H, J = 7.64 Hz), 7.63 (t, 1H, J = 7.34 Hz), 8.09 (d, 2H, J = 7.36 Hz) ppm. ^{13}C NMR: δ 104.14, 128.61, 130.26, 134.13, 135.31, 140.86, 162.92 ppm.

1-Chloroethenyl-3-methyl but-2-enoate, **2c**



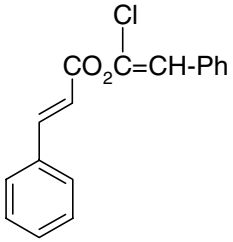
Colourless volatile liquid. IR: ν_{max} 2982 (m), 2917 (m), 1754 (s, ester C=O), 1636 (s, C=C), 1219 (s) cm^{-1}. ^1H NMR: δ 1.90 (d, 3H, J = 1Hz), 2.15 (d, 3H, J = 0.92 Hz), 4.94, 5.02 (AB quartet, 2H, J = 2.75 Hz), 5.66 (m, 1H) ppm. ^{13}C NMR: δ 20.59, 27.59, 103.46, 113.66, 140.86, 162.10, 162.61 ppm.

1-Chloroethenyl dodecanoate, **2d**



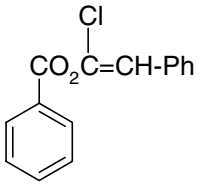
Colourless liquid. IR: ν_{max} 2924 (s), 2855 (s), 1786 (s, ester C=O), 1642 (s, C=C), 1126 (s) cm^{-1}. ^1H NMR: δ 0.88 (t, 3H, J = 6.57 Hz), 1.26 (bs, 16H), 1.68 (quintet, 2H, J = 7.26 Hz), 2.43 (t, 2H, J = 7.46 Hz), 5.01, 5.09 (AB quartet, 2H, J = 2.91 Hz) ppm. ^{13}C NMR: δ 14.04, 22.64, 24.51, 28.86, 29.12, 29.35, 29.53, 31.87, 33.77, 103.61, 140.71, 169.87 ppm. Analysis: Calculated for $C_{14}H_{25}O_2Cl$: C 64.47, H 9.66%. Found C 64.38, H 10.03%.

1-Chloro-2-phenylethenyl cinnamate, **2e**



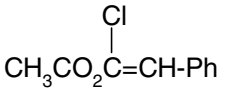
Colourless crystals (pentane), m.p. 78°C. IR: ν_{max} 3054 (w), 3028 (w), 1741 (s, ester C=O), 1635 (s, C=C), 1125 (s) cm^{-1}. ^1H NMR: δ 6.51 (s, 1H), 6.52 (d, 1H, J = 16.01 Hz), 7.27-7.44 (m, 6H), 7.56-7.62 (m, 4H), 7.87 (d, 1H, J = 16.01 Hz) ppm. ^{13}C NMR: δ 115.70, 118.52, 128.11, 128.32, 128.40, 128.78, 128.99, 131.06, 132.10, 133.73, 134.18, 148.02, 163.70 ppm. Analysis: Calculated for $C_{17}H_{13}O_2Cl$: C 71.71, H 4.60%. Found C 71.39, H 4.63%.

1-Chloro-2-phenylethenyl benzoate, **2f**



Colourless crystals (pentane), m.p. 68°C. IR: ν_{max} 3064 (w), 3027 (w), 1754 (s, ester C=O), 1645 (m, C=C), 1246 (s) cm^{-1}. ^1H NMR: δ 6.56 (s, 1H), 7.35 (m, 3H), 7.50 (m, 2H), 7.64 (m, 3H), 8.14 (d, 2H, J = 7.37 Hz) ppm. ^{13}C NMR: δ 118.73, 127.86, 128.12, 128.30, 128.61, 128.74, 130.24, 132.03, 134.08, 134.29, 163.56 ppm. Analysis: Calculated for $C_{15}H_{11}O_2Cl$: C 69.64, H 4.29%. Found C 69.76, H 4.39%.

1-Chloro-2-phenylethenyl acetate, **2g**



Colourless viscous liquid. IR: ν_{max} 3028 (m), 1782 (s, ester C=O), 1648 (m, C=C), 1186 (s), 1085 (s) cm^{-1}. ^1H NMR: δ 2.27 (s, 3H), 6.45 (s, 1H), 7.34 (m, 3H), 7.59 (m, 2H) ppm. ^{13}C NMR: δ 20.31, 118.34, 128.04, 128.19, 128.60, 131.86, 133.85, 167.52 ppm.

2-Chloroethyl dodecanoate, **6**

Colourless Liquid. IR: ν_{max} 2925 (s), 2854 (s), 1743 (s),1162 (s) cm^{-1}. ^1H NMR: δ 8.01 (t, 3H, J = 6.40 Hz), 1.19 (bs, 16H), 1.57 (m, 2H), 2.28 (t, 2H, J = 7.51 Hz), 3.61 (t, 2H, J = 5.71 Hz), 4.26 (t, 2H, J = 5.72 Hz) ppm.

2,2-Dichloroethyl dodecanoate, **7**

Colourless Liquid. IR: ν_{max} 2926 (s), 2855 (s), 1750 (s), 1151 (m) cm^{-1}. ^1H NMR: δ 0.88 (t, 3H, J = 6.27 Hz), 1.26 (bs, 16H), 1.65 (pentate, 2H, J = 7.30 Hz), 2.38 (t, 2H, J = 7.30 Hz), 4.44 (d, 2H, J = 6.02 Hz), 5.84 (t, 1H, J = 6.02 Hz) ppm.

2,2-Dichloroethyl cinnamate, **8**

Colourless Liquid. IR: ν_{max} 3029 (w), 2956 (m), 1721 (s), 1636 (s), 1157 (s) cm^{-1}. ^1H NMR: δ 4.58 (d, 2H, J = 6.01 Hz), 5.93 (t, 1H, J = 6.01Hz), 6.48 (d, 1H, J = 16.00 Hz), 7.41 (m, 3H), 7.55 (m, 2H), 7.77 (d, 1H, J = 16.00 Hz) ppm. ^{13}C NMR: δ 68.3, 68.5, 116.4, 128.2, 128.9, 130.6, 133.9, 146.4, 165.7 ppm.

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